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Resonance Enhanced Multiphoton Ionization of Molecules and Molecular Fragments

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We have completed studies of ion rotational distributions produced by resonance enhanced multiphoton ionization of excited states of molecules and by single-photon ionization of ground states of jet-cooled molecules by coherent VUV radiation. The objective of this effort was to provide a robust analysis and prediction of key spectral features of interest in related experimental studies and technological applications of these laser-driven ionization techniques.

Specific achievements include: (i) identification of underlying mechanisms for anomalous behavior of ion rotational distributions in laser ionization of molecules and molecular fragments, (ii) development of schemes for exploiting such anomalous behavior to achieve state-selective production of ions, and (iii) providing needed insight into the underlying dynamics of state-resolved molecular photoionization

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I. *Background and Objectives*

Resonance enhanced multiphoton ionization (REMPI) utilizes laser radiation to prepare a molecule in an excited state via absorption of one or more photons and to subsequently ionize that level before it decays. A remarkable feature of REMPI is that the very narrow bandwidth of laser radiation makes it possible to select a specific rotational level in the initial (ground) state and to prepare the excited state of a species of interest in a single rotational level. Thus, by suitable choice of the excitation step, it is possible to selectively ionize a species which occurs in very minor concentrations, without ionizing any other species that may be present. ***This conversion of optical selectivity into chemical selectivity makes REMPI one of the most powerful tools for ultrasensitive detection of species.*** Other applications of REMPI include its use in studies of state-selected chemistry and for exploring excited-state chemistry and physics. Coupled with high-resolution photoelectron detection, REMPI also provides ion rotational distributions for ionization of single rotational levels of excited electronic states.

Although REMPI has the distinct advantage that a single rotational level of an excited state of a molecule is ionized and that it can be achieved with photon energies less than molecular ionization potentials and consequently at more convenient wavelengths than the vacuum ultraviolet (VUV) photons required for single-photon ionization, studies of single-photon ionization of ground states of jet-cooled molecules by coherent VUV and extreme ultraviolet (XUV) radiation are highly complementary to those of REMPI. The tunable coherent radiation required for these studies can be readily produced by third-harmonic generation as well as by four-wave sum or difference frequency mixing.[1]

The objective of our work has been to carry out quantitative theoretical studies of resonance enhanced multiphoton ionization of molecules and molecular fragments and single-photon ionization of such species by coherent VUV radiation so as to provide a robust description of key spectral features of interest in related experiments and applications and needed insight into the underlying dynamics of these spectra. A major focus of our work has been on joint theoretical and experimental studies of these laser-driven ionization processes. Many of these collaborations with experimental groups in the US, Canada, and the Netherlands stem primarily from the recent development of a technique, based on the detection of threshold or zero-kinetic-energy (ZEKE) photoelectrons resulting from pulsed field ionization (PFI) of very high Rydberg states lying below an ion rotational threshold, which *makes it possible to obtain ion rovibronic state distributions with sub-wavenumber resolution.*[2] The unprecedented resolution of this technique (1 cm^{-1} or better) is opening up entirely new vistas in studies of ion spectroscopy, state-selective chemistry, and photoionization dynamics. Emerging applications built on the ultrahigh resolution of this technique include its use for accurate determination of thermochemically important ionization potentials, for characterization of ion rovibrational level structure of large organic molecules, elemental clusters, and weakly bound molecular complexes, and as a probe of nascent internal energy distributions of transient radicals.[3] This surge of experimental activity raises new theoretical challenges which have increasingly become the focus of our work.

II *Highlights of Accomplishments*

In this section I will review the progress we have made in our studies of ion rotational distributions resulting from REMPI of molecules and from single-photon

ionization of jet-cooled molecules by coherent VUV and XUV radiation. This review is not intended to be exhaustive but to highlight the significance of our objectives and accomplishments and to illustrate the insight our studies provide.

Although we will not discuss the quantum mechanical formulation and computational procedures used to obtain the molecular photoelectron orbitals and photoionization matrix elements needed in these studies,[4] it is essential to recognize that the rotationally state-selective studies of interest here require the use of molecular photoelectron orbitals which correctly incorporate the angular momentum coupling present in these orbitals. In contrast to atomic photoelectron orbitals, molecular photoelectron orbitals are not angular momentum eigenfunctions but contain admixtures of angular momenta. This coupling of angular momenta is brought about by the torques associated with the nonspherical potentials of molecular ions in which the photoelectron moves. This simply reflects the fact that as the photoelectron scatters off the ion core, its angular momentum (ℓ) as well as that of the ion core (J) changes. These angular-momentum changing collisions between the photoelectron and the ion clearly play a crucial role in determining ion rotational distributions.

In these studies the molecular photoelectron orbitals are obtained as solutions of a one-electron Schrödinger equation containing the Hartree-Fock potential of the molecular ion V_{ion}, (r, R),

$$(-\frac{1}{2}\nabla^2 + V_{ion}(\mathbf{r}, R) - \frac{k^2}{2})\psi^{(-)}_{k\ell m}(\mathbf{r}, R) = 0, \qquad (1)$$

where $\psi^{(-)}_{k\ell m}$ is a partial wave component of the photoelectron orbital $\Psi^{(-)}_k$. The $\psi^{(-)}_{k\ell m}$ satisfy scattering boundary conditions and must be obtained numerically. We actually obtain these orbitals using an iterative procedure, based on the Schwinger variational principle, to solve the integral equation associated with eq. (1).[4] The

procedure is numerically stable even at the very low photoelectron energies ($\sim$ 0.05 eV) often of interest in these studies.

(a) *Resonance Enhanced Multiphoton Ionization of Molecules and Fragments*

As our first example we look at the rotational distributions of ions for (2+1) REMPI of the NH and OH radicals.[5,6] Fig. 1 shows (a) measured and (b) calculated rotationally resolved photoelectron spectra along with (c) calculated photoelectron angular distributions for (2 + 1) REMPI via the R(12) branch of the $f^1\Pi$ ($3p\sigma$) state of NH for the $v^+ = 0$ and 1 levels of the ion. In these spectra the spin-orbit components of the $X\ ^2\Pi$ state of NH^+ and the parity components of the resonant and ionic states are not resolved. The calculated spectrum is also convoluted with a Gaussian detection function having a full-width at half-maximum (FWHM) of 30 meV. The most striking feature of these spectra is the appearance of strong $\Delta N = N^+ - N =$ *even* peaks, particularly for $\Delta N = 0$, for photoionization of this $3p\sigma$ Rydberg orbital of NH. On the basis of the simple selection rule $\Delta N + \ell$ = odd,[6] these even ΔN (= 0,$\pm$ 2) peaks must be associated with odd (ℓ = 1,3) angular momentum components of the photoelectron matrix element. With its 67% p character one would expect significant contributions from the $\ell = 0$ and 2 components of the photoelectron matrix element for ionization of this $3p\sigma$ Rydberg orbital and hence strong odd ΔN peaks.

It is clearly important to identify the underlying dynamical reason for the unusual behavior seen in these ion rotational distributions. Detailed calculations of these rotational distributions show that the strong even ΔN peaks in these spectra are, in fact, due to the presence of a Cooper minimum in the $\ell = 2$ component

of the photoionization matrix element.[6] Such a Cooper minimum occurs at a photoelectron kinetic energy where a specific angular monentum component of the photoionization matrix element changes sign and goes through a zero. These angular momentum components of the photoelectron matrix element are essentially

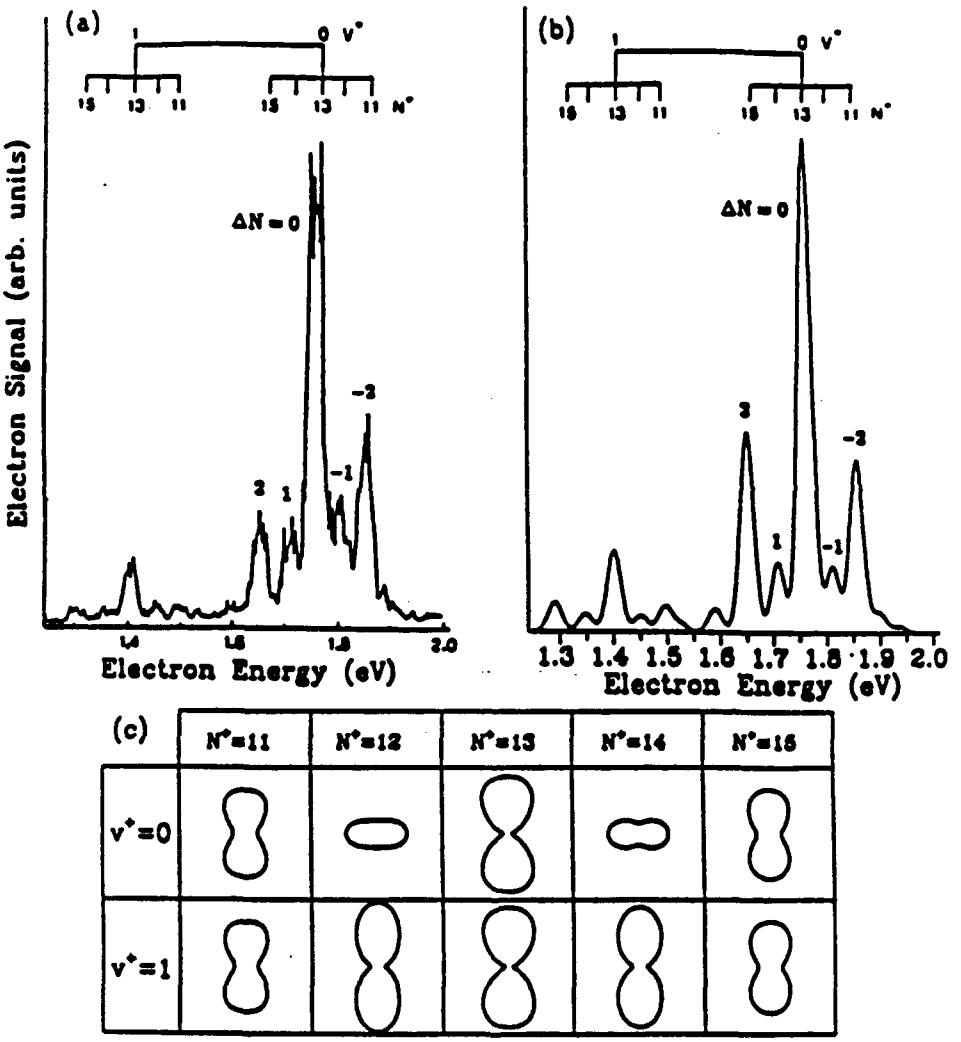

Fig. 1 (a) measured and (b) calculated photoelectron spectra along with the (c) calculated photoelectron angular distributions for (2 + 1) REMPI via the R(12) branch of the $f^1\Pi$ ($3p\sigma$) state of NH for the $v^+ = 0$ and 1 vibrational bands. The measured spectra are taken from ref. 5.

the driving force for ejection of the photoelectron with a specific angular momentum ℓ. At a Cooper minimum a specific ℓ component of this driving force is diminished and hence corresponding ion rotational peaks, which are related to ℓ through $\Delta N + \ell = odd$, are weakened. Here depletion of the d wave ($\ell = 2$) contributions to the photoelectron matrix element in the vicinity of the Cooper minimum weakens the $\Delta N = odd$ peaks and subsequently enhances the relative importance of the odd components ($\ell = 1$ and 3) of this matrix element and, hence, that of the even ΔN rotational peaks.

Fig. 1 (c) shows the calculated photoelectron angular distributions for the ion rotational levels in the spectrum of fig. 1. A significant feature of these spectra is that the angular distributions for the $\Delta N = \pm 1$ peaks ($N^+ = 12$ and 14) are quite different for the $v^+ = 0$ and 1 levels of the ion. This behavior is due to a dependence of the photoelectron matrix element on internuclear distance which, in turn, arises from a rapid evolution the $3p\sigma$ orbital of the $f^1\Pi$ state from predominant 3p character at smaller internuclear distance to 3s character at larger R. It is surprising that this dependence is so evident for such low vibrational excitation.

Fig. 2 shows measured and calculated rotationally resolved photoelectron spectra for (2 + 1) REMPI of OH via the O_{11} (11) branch of the $D\,^2\Sigma^-$ ($3p\sigma$) [figs. 2 (a) and 2 (b)] and the $3\,^2\Sigma^-$ ($4s\sigma$) [figs. 2 (c) and 2 (d)] Rydberg states.[7] These spectra again serve to demonstrate the significant influence that Cooper minima exert on ion rotational distributions. Cooper minima have been predicted to occur in the d ($\ell = 2$) wave of the kσ and kπ continua for photoionization of the $D\,^2\Sigma^-$ Rydberg state but not in the $3\,^2\Sigma^-$ state. The presence of these Cooper minima for the $D\,^2\Sigma^-$ state accounts for the occurrence of strong $\Delta N = even$ signals in the photoelectron spectrum in contrast to the ΔN = odd distribution expected for ionization

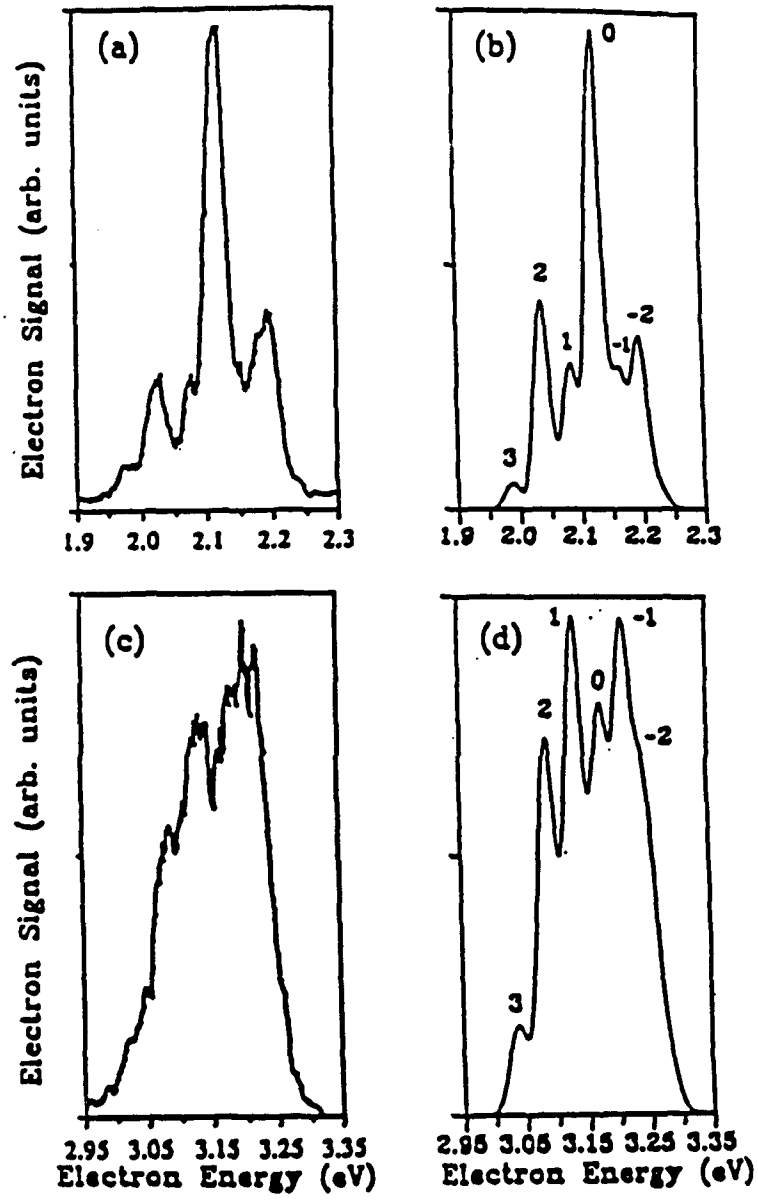

Fig. 2. Experimental and calculated rotationally resolved photoelectron spectra for (2 + 1) REMPI of OH: (a) measured spectrum for the $D\ ^2\Sigma^-$ photoelectron spectrum, assuming a Gaussian line shape with an FWHM of 30 meV; (c) measured spectrum for the $3\ ^2\Sigma^-$ $(4s\sigma)$ state, $v = 0 \rightarrow v^+ = 0$, O_{11} (11) rotational branch; (d) calculated $3\ ^2\Sigma^-$ $(4s\sigma)$ photoelectron spectrum assuming a Gaussian line shape with a FWHM of 35 meV. The labelling of peaks in the calculated spectra indicates the change of rotational quantum number $\Delta N = N^+ - N$.

of a 3pσ Rydberg orbital in an atomiclike picture, i.e., 3p$\sigma \rightarrow$ ks, kd photoionizing transitions. On the other hand, the photoelectron spectra for photoionization of the $3\,^2\Sigma^-$ (4sσ) state of figs. 2(c) and 2(d) reveal a qualitatively different and much broader distribution with prominent ΔN = even and ΔN = odd transitions. The appearance of these spectra arises from greater ℓ-mixing in this higher Rydberg orbital (54% s and 43% p character at R = 2.043 a_o).

Cooper minima can be expected to have far-reaching and wide-spread implications for the behavior of ion rotational distributions. For example, similar effects in ion rotational distributions due to Cooper minima have also been predicted for H_2O and SiF. Furthermore, Cooper minima can also be exploited to achieve a high degree of rotational selectivity in ion rotational distributions.[8]

We have also studied the rotational distributions of HBr^+ ions in their $X\,^2\Pi_{1/2}$ ground state for (2 + 1) REMPI of HBr via the S(2) branch of the $F\,^1\Delta_2$ (5pπ) Rydberg state.[9] These studies were motivated by the measurements of Xie and Zare in which the populations of the individual parity components of each ion rotational level were obtained using laser-induced fluorescence.[10,11] Such measurements of ion populations for individual parity components of a Λ doublet provide a very stringent test of the underlying angular momentum make-up of molecular photoelectron wave functions.[9,10] These spectra show a strongly (−) parity-favored ion rotational distribution for photoionization of the (+) parity component of the J = 4 level of the 5pπ Rydberg orbital of the $F\,^1\Delta_2$ state which has about 97% p (ℓ = 1) character. These (−) parity-favored ion distributions can be readily understood on the basis of parity selection rules[12,13] and the dominance of the photoelectron matrix element by its ℓ = 0 and 2 angular momentum components for photoionization

of this 5pπ Rydberg orbital with its 97% p character. Fig. 3 compares our calculated

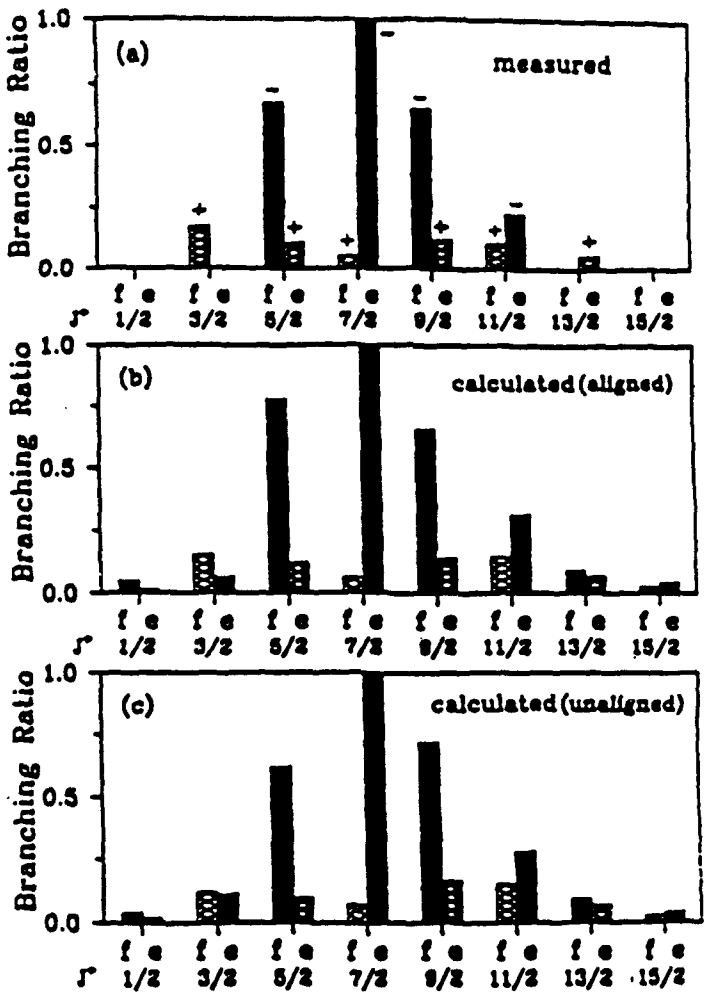

Fig. 3. Rotational distributions of HBr^+ for (2 + 1) REMPI via the S(2) branch of the $F\ ^1\Delta_2$ state: (a) measured distributions of ref. 16; (b) and (c) calculated distributions of ref. 9 for the aligned and unaligned resonant states, respectively.

ion rotational distributions with the measured spectra of Xie and Zare.[6] The photoelectron energy is about 2.33 eV. Calculated spectra are shown for photoionization of both the optically aligned J = 4 level (fig. 3(b)) and an unaligned J = 4 level

(fig. 3(c)). The agreement between the calculated and measured ion distributions is very encouraging.

Note that, on the basis of parity selection rules,[12,13] the 20% population seen in the (+) parity component (cross-hatched bars) of the doublet *must be due to odd partial wave components of the photoelectron matrix element which arise from angular momentum coupling in the molecular photoelectron.* Examination of the photoelectron matrix elements reveals that the $\tilde{i}$ wave of the $5p\pi \rightarrow k\delta$ ionization channel makes the dominant contribution to the population of these (+) parity levels of the ion.[9] Such behavior is entirely nonatomic-like. Comparison of the ion distributions for the unaligned J = 4 level with those for an optically aligned J = 4 level and with the measured spectra serves to illustrate that, although not large, the effect of alignment can be important.

(b) *Threshold Photoionization of Linear Molecules*

We now highlight the progress we have made in our studies of ion rotational distributions for single-photon ionization of diatomic molecules and fragments by coherent VUV and XUV radiation. In contrast to the spectra discussed above where the photoelectron energies were of the order of 1 to 2 eV, we now look at ion rotational distributions for threshold photoionization where the photoelectron energy is essentially zero. The measured spectra with which our calculated ion rotational distributions will be compared in the two examples have been obtained using a technique based on the detection of zero-kinetic-energy (ZEKE) photoelectrons resulting from pulsed-field ionization (PFI) of very high Rydberg states lying below a rotational threshold.[2] This ZEKE-PFI technique makes it possible to obtain ion rovibronic state distributions with sub-wavenumber resolution. Although

these ZEKE techniques are limited to measurements of threshold photoionization cross sections, *this dramatic improvement in resolution over that of conventional photoelectron certainly opens up new possibilities for studying photoionization dynamics, ion spectroscopy, and state-selected ion-molecule reactions.* In fact, several novel applications built on the ultra-high resolution of this technique have already emerged.[14] Measurements of ion rotational distributions for very low rotational levels and at threshold photoelectron energies, which this technique makes possible for a wide range of molecules, can certainly be expected to raise important theoretical challenges and to provide significant insight into the coupling of electronic and nuclear motion inherent in the photoionization process.

Fig. 4 shows the (a) measured and (b) our calculated ZEKE photoelectron spectra for single-photon ionization of rotationally cold NO $X\ ^2\Pi_{1/2}, (v'' = 0)$ molecules leading to NO^+ $(X\ ^1\Sigma^+, v^+ = 1)$ by coherent VUV radiation.[15] The calculated ion rotational distributions assume a temperature of 5 K. These spectra were calculated for a photoelectron energy of 50 meV and convoluted with a Gaussian detection function with an FWHM of 2 cm^{-1}. In this figure each branch is associated with a letter designation which refers only to the change in angular momentum apart from spin, i.e., $\Delta N = N^+ - N''$. The label 1′ denotes the $N'' = 1$, $J'' = 1/2$ level. The agreement between these measured and calculated spectra is excellent.

To provide further insight into the underlying dynamics of these threshold photoelectron spectra, fig. 5 (a) and (b) show measured and calculated ion rotational branching ratios for photoionization of the $N'' = 1$, $J'' = 3/2$ rotational level of the $X\ ^2\Pi_{1/2}$ ground state of NO. The data of fig. 5 (a) is extracted from

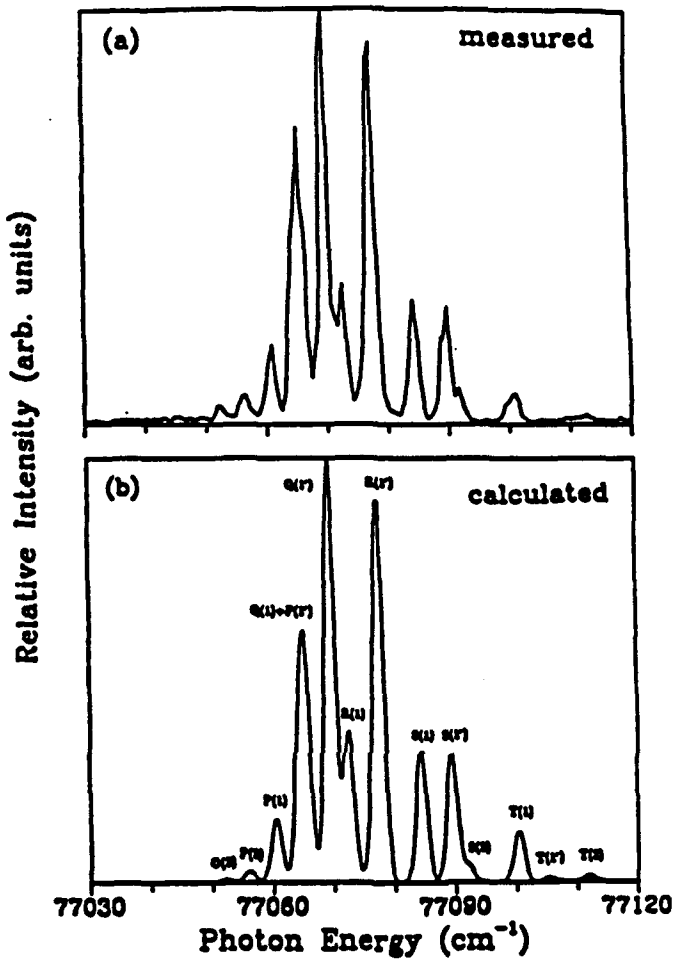

Fig. 4. (a) measured and (b) calculated ZEKE photoelectron spectra for single-photon ionization of rotationally cold NO ($X\ ^2\Pi_{1/2}$) by coherent VUV radiation. The calculated spectrum is for 5 K.

the measured photoelectron spectrum of fig. 4 (a) for rotationally cold NO where, in addition to the N'' = 1 level, a few other rotational levels are also populated. These rotational branching ratios for ionization of this valence 2π orbital differ somewhat from those generally seen in ZEKE spectra of Rydberg states. This behavior reflects the broad range of angular momentum components ($\ell = 0$, 1, 2, and 3) which

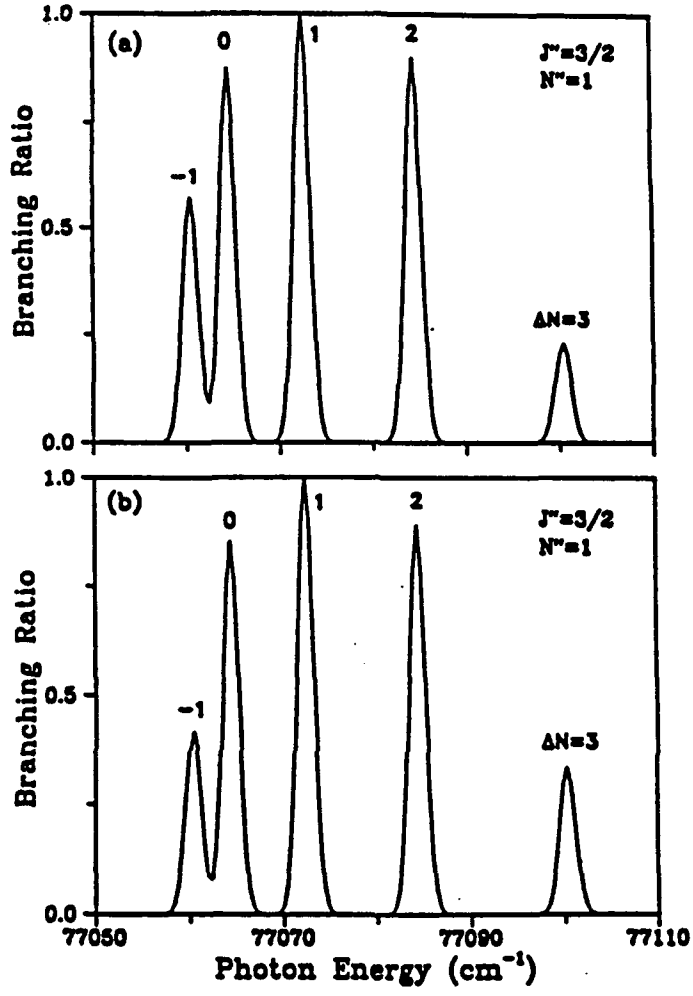

Fig. 5 (a) measured and (b) calculated ZEKE photoelectron spectra for single-photon ionization of the $N'' = 1, J'' = 3/2$ level of the $X^2\Pi_{1/2}$ state of NO by coherent UVU radiation.

make significant contributions to the photoelectron matrix element for this valence orbital. Unusually strong s and d waves are predicted in addition to the p and fpartial waves expected for photoionization of the 2π orbital with its 85% d ($\ell = 2$) character. These s and d components of the photoionization matrix element are due to angular momentum coupling in the molecular photoelectron wavefunction.

Fig. 6 shows the ZEKE photoelectron spectra for single-photon ionization of rotationally cold CO ($X\ ^1\Sigma^+$) molecules by coherent XUV radiation.[16] These jet-cooled PFI spectra are for the $v^+ = 0$ level of CO^+ ($X\ ^2\Sigma^+$). The calculated spectra assume a temperature of 8 K and a photoelectron energy of 50 meV and are convoluted with a Gaussian detection function with an FWHM of

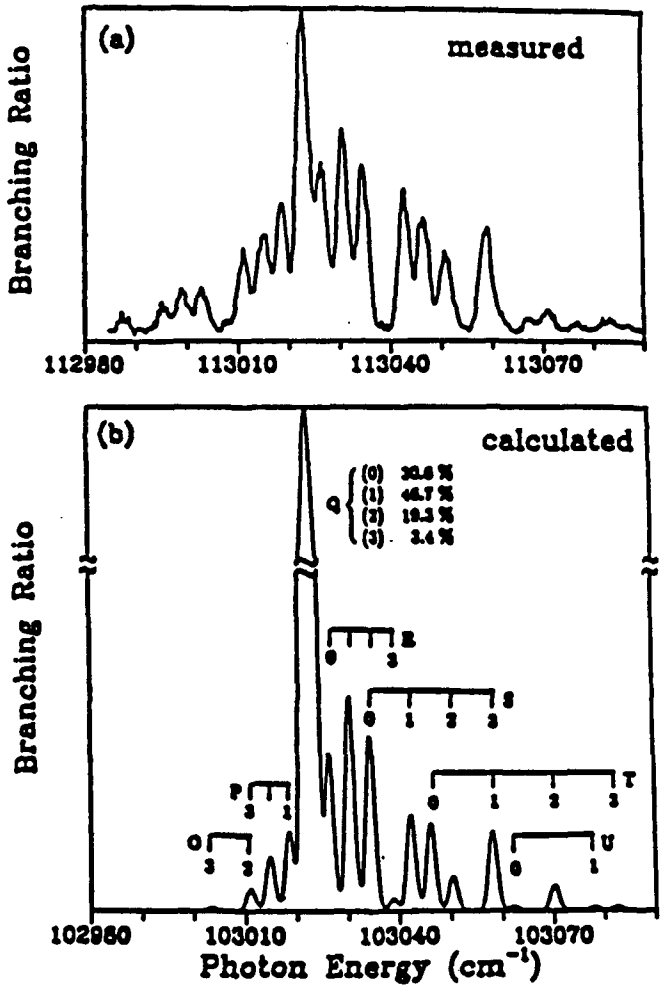

Fig. 6. (a) measured and (b) calculated ZEKE photoelectron spectra for single-photon ionization of rotationally cold CO ($X\ ^1\Sigma^+$) by coherent XUV radiation. The calculated spectrum is for 8 K.

2 cm^{-1}. The letter designation on each branch refers only to the change of angular momentum apart from spin. The agreement between these calculated and measured rotational branching ratios is excellent for all branches except the Q (Δ N = 0) branch. This behavior is indicated by the broken scale in fig. 6(b). The strength of the Q branches in these spectra is consistent with the parity selection rule, $\Delta N + \ell$ = odd,[12] and the atomiclike behavior for photoionization of the 5σ orbital (45% s and 25% d character). The origin of this disagreement between these calculated and measured spectra is not yet clear.

(c) *Threshold Photoionization of Nonlinear Molecules*

Fig. 7 (a) shows the rotationally resolved ZEKE pulsed-field ionization spectrum of H_2O recently reported by Tonkyn et al. for single-photon ionization of the $1b_1$ orbital by coherent VUV radiation[17]. This spectrum can be assigned to two types of rotational transitions, corresponding to specific changes in the asymmetric top angular momentum projection quantum numbers K_a and K_c. Most of the strong spectral lines could be classified as type c rotational transitions (ΔK_a = odd, ΔK_c = even), but type a transitions (Δ K_a = *even*, Δ K_c =*odd*) are also clearly evident. Fig. 7(b) shows our calculated ion rotational distributions for photoionization of the $1b_1$ orbital of the $\tilde{X}\,^1A_1$ ground state of jet-cooled H_2O leading to the $\tilde{X}\,^2B_1$ (000) state of the ion.[18] A rotational temperature of 15 K is assumed in these calculations. Furthermore, we assume that there is no spin exchange taking place during the jet-cooled expansion of room-temperature water. The calculated spectrum is convoluted with a Gaussian detection function with an FWHM of 1.5 cm^{-1}. The agreement between the calculated and measured spectra is clearly encouraging except for the calculated $0_{00} \rightarrow 2_{12}$ transition which is somewhat stronger than that

of the measured value.

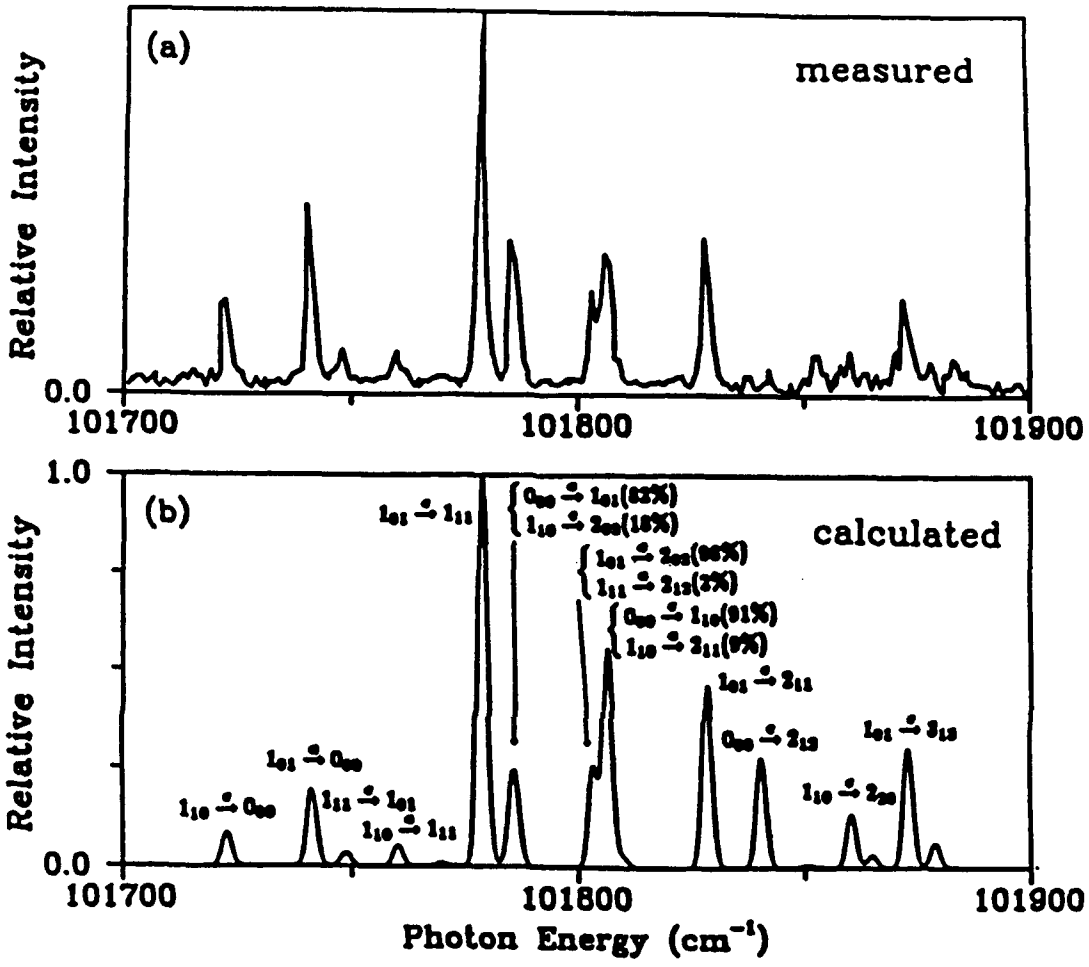

Fig. 7. (a) measured and (b) calculated ion rotational distributions for photoionization of the $1b_1$ orbital of the $\tilde{X}\ ^1A_1$ ground state of jet-cooled H_2O. The *a* and *c* labels indicate type *a* and type *c* transitions, respectively.

The underlying dynamics of these photoelectron spectra is quite rich. We have shown that parity selection rules require that[15,19]

$$\Delta K_a + \ell = odd, \tag{2}$$

and

$$4\mu + \lambda = \Delta K_b, \tag{3}$$

where μ is the photon polarization index in the molecular frame and λ is the projection of ℓ, the angular momentum of the photoelectron, in the molecular frame.[19] Eqs. (2) and (3) assume that the molecular z axis coincides with the C_2 symmetry axis and the x axis lies in the plane of the molecule. The molecular x, y, and z axes hence coincide with the a, c, and b axes, respectively. Since $\mu + \lambda$ is always odd for photoionization of the $1b_1$ orbital of H_2O, it can be shown that[19]

$$\Delta K_a + \Delta K_c = odd. \tag{4}$$

Both type *a* and type *c* transitions are allowed and type b [ΔK_a = even (odd) and ΔK_a = even (odd)] transitions are forbidden. Furthermore, eq. 2 shows that ***type a transions*** ($1_{01} \rightarrow 0_{00}, 0_{00} \rightarrow 1_{01}, 1_{01} \rightarrow 2_{02}$, and $1_{11} \rightarrow 2_{12}$) ***arise from odd (almost pure p) wave contributions to the photoelectron matrix element.*** These p waves of the ka_1 and kb_1 continua are entirely molecular in origin since the almost p (99.7%) character of the $1b_1$ orbital of water leads only to s and d photoelectron continua in an atomiclike picture. The strong type *c* transitions in the spectra of fig. 7 arise from s and d (even) components of the photoelectron matrix element.

Figure 8 shows the (a) measured[20] and (b) calculated[21] rotationally resolved ZEKE-PFI spectra of $CH_3(\tilde{X}\,^2A_2'')$ for single-photon ionization of the $1a_2''$ orbital by coherent VUV radiation leading to the $\tilde{X}\,^1A_1'$ ground state of the ion. The calculated spectrum assumes a rotational temperature of 250 K and a photoelectron kinetic energy of 50 meV and is convoluted with a Gaussian detection function with an FWHM of 2.5 cm^{-1}. The CH_3 and CH_3^+ are oblate symmetric tops , belonging to the D_{3h} point proup. For the D_{3h} group, the *total* wave function of CH_3 should

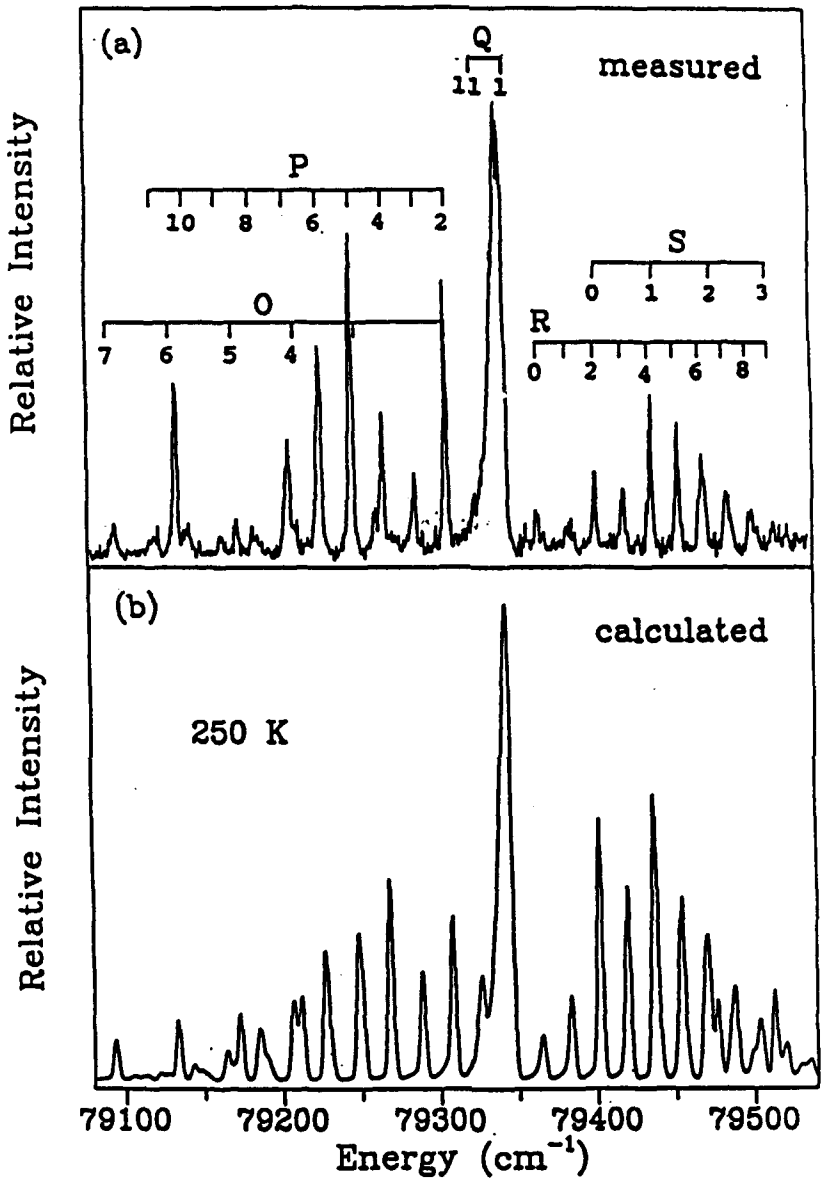

Fig. 8 (a) measured and (b) calculated ion rotational distributions for single-photon ionization of the $1a_2''$ orbital of the $\tilde{X}\ ^2A_2''$ ground state of jet-cooled CH_3 leading to the $\tilde{X}\ ^1A_2'$ ground state of the ion. The calculated spectrum is for 250 K and has an FWHM of 2.5 cm^{-1}.

have either A_2' or A_2'' symmetry in order to satisfy the Pauli principle. The wave functions for ortho and para species have A_1' (I = 3/2) and E' (I = 1/2) symmetries,

respectively. Since $\Gamma_{spin} \otimes \Gamma_{rot} \supset \Gamma_{total}$, the rotational wave function must have A_2', A_2'', E', or E'' symmetry. Therefore, the rotational levels belonging to A_1' and A_1'' symmetries are not initially populated, i.e., levels with $J = even$, K = 0 and the A_1 (K = $3n$) level of the $A_1 - A_2$ pair are forbidden. Due to the spin statistical weigth of 4:2 between ortho and para species, the $K = 3n + 1$ levels (A_2' or A_2'') have a statistical weight twice that of the K = 3 n + 1 levels (E′ or E″).

Agreement between the calculated and measured spectra is very encouraging in spite of some discrepancies due to rotational autoionization at negative ΔN transitions. Our calculations reveal that ΔK = 0 are the dominant transitions (up to 95%) and the ΔK = ± 2 (not labeled) transitions are much weaker. Even though the ΔK = *odd* transitions are also dipole-allowed, their intensities are very weak and they do not appear in the spectrum. Note that ΔK = *odd* transitions are associated with $\mu + \lambda = odd$ partial waves of the photoelectron, which, in turn, must originate from the f ($\ell_0 = 3$) component of the $1a_2''$ orbital of the ground state. Since the $1a_2''$ orbital is essentially an out-of-plane $2p$ orbital localized on the central carbon atom, its f wave is negligible. This leads to a Δ K = *even* selection rule.

Figure 9 shows the (a) measured and (b) calculated rotationally resolved ZEKE-PFI spectra of H_2CO for single-photon ionization of the nonbonding $2b_2$ orbital by coherent VUV radiation.[21] The calculated spectrum assumes a rotational temperature of 7 K and a photoelectron kinetic energy of 50 meV and is convoluted with a Gaussian detection function with an FWHM of 1.8 cm^{-1}. Furthermore, we assume that no spin exchange takes place during the jet-cooled expansion of room-temperature formaldehyde, i.e., a population ratio of 2:1 is kept for the ortho (B

symmetry) to para (A symmetry) species. The agreement between calculated and measured spectra is very encouraging.

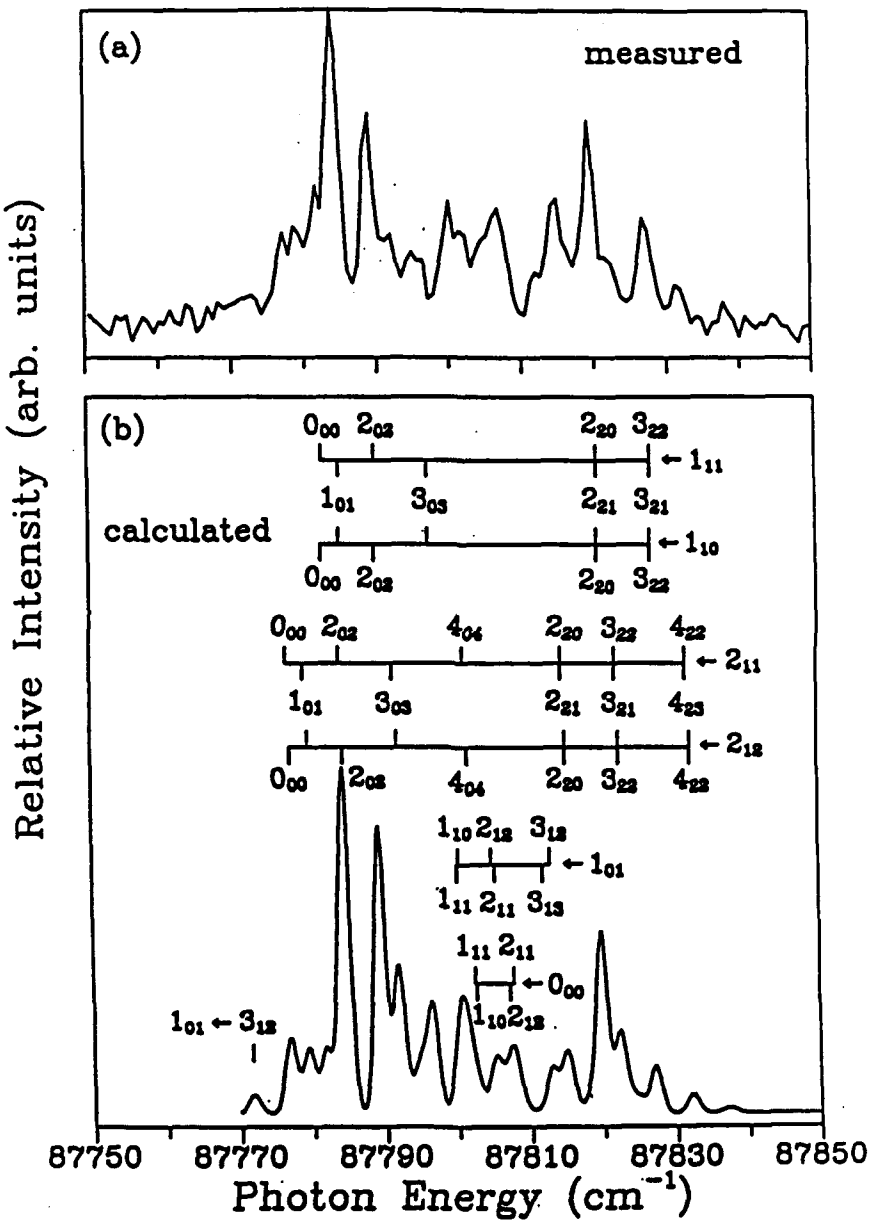

Fig. 9 (a) measured and (b) calculated ion rotational distributions for single-photon ionization of the $2b_2$ orbital of the $\tilde{X}\ ^1A_1$ ground state of jet-cooled H_2CO. The calculated spectrum is for 7 K and has an FWHM of 1.8 cm^{-1}.

In our calculations we assume that the molecular z axis coincides with the C_2 symmetry axis and the x axis lies in the plane of the formaldehyde molecule (ion). The molecular x, y, and z axes hence coincide with the b, c, and a axes, respectively. From the parity selection rules we obtain

$$\Delta K_b + \ell = odd, \tag{5}$$

and

$$\mu + \lambda = \Delta K_a. \tag{6}$$

From photoionization of the $2b_2$ orbital of H_2CO, $\mu + \lambda$ is always odd and, hence, we have

$$\Delta K_b + \Delta K_c = odd. \tag{7}$$

Clearly, both type *c* ($\Delta K_a = odd$ and $\Delta K_c = even$) and type *b* ($\Delta K_a = odd$ and $\Delta K_c = odd$) transitions are allowed and type *a* ($\Delta K_a = even$ and $\Delta K_c = odd$) and other type *b* ($\Delta K_a = even$ and $\Delta K_c = even$) transitions are forbidden. Furthermore, Eqns. (5-7) show that the allowed type *b* transitions arise from odd partial wave contributions to the photoelectron matrix elements whereas the type *c* transitions arise from even angular momentum components of the photoelectron.

In Fig. 9 (b), we label several of the more important transitions out of rotational levels of the ground state of the neutral species leading to different rotational levels of the ion. The quantum numbers used as labels are $N_{K_aK_c}$. Note that in this figure we use the same set of quantum numbers to designate type *c* transitions out of the 1_{11} level and type *b* transitions out of the 1_{10} level, since the energies of these transitions are essentially equal. A similar labeling is also adopted for transitions out of the 2_{11} and 2_{12} rotational levels. Since the moments of inertia I_b and I_c are almost the same for H_2CO (H_2CO^+), the rotationally resolved ZEKE-PFI spectra

are very congested. Unlike the spectra for H_2O, type *b* transitions, which arise from odd waves, cannot be distinguished from type *c* transitions, which arise from even waves.

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III *The research highlighted above has resulted in the following publications:*

1. *Rotationally Resolved Photoionization of Polyatomic Hydrides: CH_3, H_2O, H_2S, H_2CO*

   R.T. Wiedmann, M. White, K. Wang, and V. McKoy

   J. Chem. Phys. **100**, 4738 (1994)

2. *Rotationally Resolved Threshold Photoelectron Spectroscopy of H_2O and H_2S*

   K. Wang, M.-T. Lee, V. McKoy, R.T. Wiedmann, and M. White

   Chem. Phys. Lett. **219**, 397 (1994)

3. *Studies of Photoionization Dynamics of CH, NH, and OH Radicals at Near-Threshold Photoelectron Kinetic Energies*

   K. Wang, J.A. Stephens, and V. McKoy

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4. *Pulsed-Field Ionization Threshold Photoelectron Spectroscopy with Coherent XUV Radiation: A Comparison of CO and N_2*

   W. Kong, D. Rodgers, J.W. Hepburn, K. Wang, and V. McKoy

   J. Chem. Phys. **99**, 3159 (1993)

5. *Energy Dependence of Photoion Rotational Distributions of N_2 and $C^{\prime}$)*
Heung Cheun Choi, R.M. Rao, A.G. Mihill, Sandeep Kakar, E.D. Poliakoff, K. Wang, and V. McKoy
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6. *Spin-Orbit Autoionization and Intensities in the Double-Resonant Delayed Pulsed-Field Threshold Photoionization of HCl*
Y.-F. Zhu, E.R. Grant, K. Wang, and V. McKoy
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7. *Rotationally Resolved Photoelectron Spectra in (2+1) Resonance Enhanced Multiphoton Ionization of NO via the $C\,^2\Pi$ Rydberg State*
K. Wang, V. McKoy, and H. Rudolph
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8. *Rotationally Resolved Photoelectron Spectra at Near-Threshold Kinetic Energies*
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9. *Ion Rotational Distributions for Nonlinear Molecules at Near-Threshold Photoelectron Energy*
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11. *Rotational State-Selective Photoionization Dynamics of Molecules at Near-Threshold Photoelectron Energies*
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J. Phys. Chem. **97**, 9874 (1993)

12. *Rotational Analysis of the HeI Photoelectron Spectrum of HF*
K. Wang, V. McKoy, M.-W. Ruf, A.J. Yencha, and H. Hotop
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13. *Studies of Molecular Rydberg States by Schwinger Variational-Quantum Defect Methods: Application to Molecular Hydrogen*
J.A. Stephens and V. McKoy
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14. *Ion-Rotational Distributions at Near-Threshold Photoelectron Energies*
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10th VUV Conference, (Paris, July 27-31, 1992),edited by
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15. *Rotationally Resolved Photoelectron Spectra in Resonance Enhanced Multiphoton Ionization of SiF*
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21. *Rotationally Resolved Photoelectron Spectra in Resonance Enhanced Multiphoton Ionization of HCl via the $f\ ^1\Delta_2$ Rydberg State*
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22. *Rotationally Resolved Photoionization of Molecular Oxygen*
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23. *Rotational Branching Ratios and Photoelectron Angular Distributions in Resonance Enhanced Multiphoton Ionization of HBr via the $f\ ^1\Delta_2$ Rydberg State*
K. Wang and V. McKoy
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24. *Effects of Cooper Minima in Resonance Enhanced Multiphoton Ionization Photoelectron Spectroscopy of NO via the $D\ ^2\Sigma^+$ and $C\ ^2\Pi$ Rydberg States*
K. Wang, J.A. Stephens, and V. McKoy
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25. *Rotational Branching Ratios and Photoelectron Angular Distributions in Resonance Enhanced Multiphoton Ionization of Diatomic Molecules*
K. Wang and V. McKoy
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26. *Rotationally Resolved Photoelectron Spectroscopy of the $^2\Sigma^-$ Rydberg States of OH: The Role of Cooper Minima*

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and V. McKoy
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27. *Cooper Minima and Circular Dichroism in Photoelectron Angular Distributions*
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29. *Orbital Evolution and Promotion Effects in the Photoionization Dynamics of $^2\Sigma^-$ Rydberg States of OH*
J. A. Stephens and V. McKoy
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30. *Shape Resonance Effects in the Rotationally Resolved Photoelectron Spectra of O_2*
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H. Rudolph and V. McKoy
J. Chem. Phys. **93**, 7054 (1990)

IV *Seminars and invited letures presented on the studies oulined above include:*

1. Invited speaker at the Gordon Research Conference on Multiphoton Processes, June 1990, Colby-Sawyer Junior College, New Hampshire

2. Invited speaker at the European Research Conference on Very High Resolution Spectroscopy with Photoelectrons–ZEKE Spectroscopy, October 1991, Kreuth, Germany.

Note: The European Research Conferences are Gordon-like Research Conferences sponsored by the European Science Foundation and the Commission of the European Communities.

3. Invited Speaker at the 10th International Conference on Vacuum Ultraviolet Radiation Physics, July 1992, Paris, France

4. Invited Speaker at the International Workshop on Photoionization, August 1992, Berlin, Germany.
   Note: This Workshop is a ***by-invitation-only*** meeting covering significant developments in the field.

5. Invited Speaker at the annual meeting of the Division of Atomic, Molecular, and Optical Physics of the American Physical Society, May 1993, Reno, Nevada

6. Invited Speaker at the SPIE Laser Symposium on Techniques for State-Selected and State-to-State Chemistry, January 1993, Los Angeles, California

7. Invited Speaker at the European Research Conference on Very High Resolution Spectroscopy with Photoelectrons: Excited State Spectroscopy and Dynamics, September 1993, Giens, France

8. Plenary Speaker at the Sanibel Symposium on Photoinduced Phenomena, March 1992, St. Augustine, Florida

9. Colloquium Speaker at the University of Nebraska, Lincoln, Nebraska, September 1991

10. Colloquium Speaker at Louisiana State University, Baton Rouge, Louisiana, February 1992

11. Colliquium Speaker at the University of Waterloo, Waterloo, Ontario, June 1993

12. Distinguished Lecture Series: Frontiers in Chemical Research, Texas A&M University, December 1993

13. Colloquium Speaker at Tulane University, New Orleans, Louisiana, April 1994

14. Invited Speaker at the European Workshop on Ion Spectroscopy, Tegernsee, Germany, September 1994

15. Invited Speaker at the International Workshop on Photoionization, San Francisco, California, October 1994

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Matthew Braunstein (1990-91)

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J. A. Stephens

K. Wang